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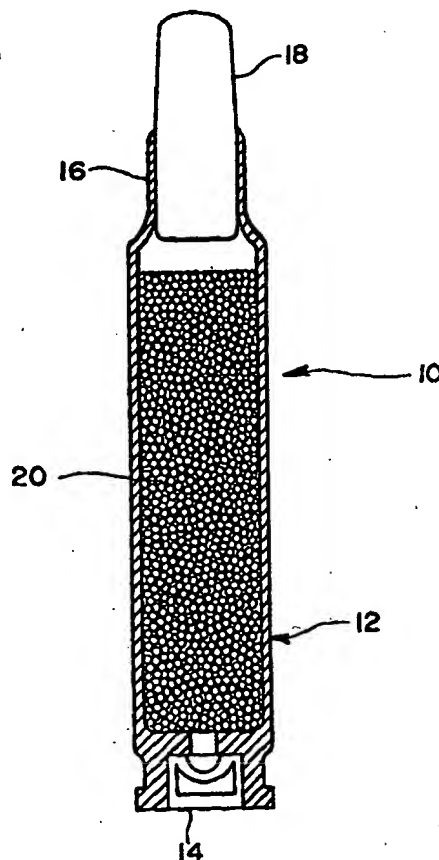
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Title: NON-LEAD, ENVIRONMENTALLY SAFE PROJECTILES AND METHOD OF MAKING SAME

Abstract

A projectile, such as a bullet (18), is made by combining two different metals in proportions calculated to achieve a desired density, without using lead. A base constituent, made of a material having density greater than lead, is combined with a binder constituent having a less density. The binder constituent is malleable and ductile alloy phase material that forms projectile shapes when subjected to a consolidation process, such as compression. The metal constituents can be selected, rationed, and consolidated to achieve desired frangibility characteristics.



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NON-LEAD, ENVIRONMENTALLY SAFE PROJECTILES  
AND METHOD OF MAKING SAME

5 This invention was made with government support under Contract No. DE-AC05-840R21400 awarded by the U.S. Department of Energy to Martin Marietta Energy Systems, Inc. and the government has certain rights in this invention.

FIELD OF THE INVENTION

10 The present invention relates generally to powder metallurgy, and more specifically, to projectiles or other objects made from consolidated powdered materials. The materials are chosen to emulate or improve upon the mechanical properties and mass of lead.

15 DESCRIPTION OF THE RELATED ART

Bullets are a type of projectile which have relied on the density of lead to generate a desirable force, commonly measured in foot pounds of energy, when propelled at a desired velocity.

20 One type of bullet includes a lead core jacketed with copper. This type of construction and combination of materials has been used successfully because the density of lead produces desirable ballistic performance.

25 Moreover, the ductility and malleability of lead

makes it easily worked into projectile shapes, and produces desirable impact deformation.

5       Lead-containing bullets present both environmental and safety problems, when fired at practice ranges. Health issues arise from breathing airborne lead contaminants generated from firing the projectiles impact on the projectiles. Environmentally, lead from the projectiles fired at an outdoor range  
10       accumulates in the ground and can leach into surface water and ground water. In terms of safety, projectiles fired indoors or outdoors can ricochet and thereby cause unintended collateral damage.

15       The safety, health and environmental issues with regards to the firing of projectiles at ranges and other training facilities (or in general, any training exercise where projectiles are fired into the environment) have prompted  
20       the development and evaluation of alternative ammunition that eliminates the undesirable health, safety and environmental aspects of lead.

      It has not been a simple matter to replace  
25       lead as a material for making projectiles. Alternative projectiles considered in the past have not been able to maintain the mechanical and physical properties of lead so as to achieve comparable performance. For example, the  
30       ability of the projectile to retain its velocity and energy is measured by its sectional density is proportional to the projectile mass divided by the square of the caliber. Thus, it is seen that a projectile of low mass or density will  
35       not retain its velocity and energy as well as a projectile of higher mass and energy.

Recent efforts to replace lead in bullets have focused on powdered metals with polymer binders, plastic or rubber projectiles, and bismuth metal. However, these replacements have yet to meet all desired specifications and performance goals.

At the end of World War II, projectiles used in 50 caliber weapons for training, and to replace lead, were fabricated from tungsten, iron, and bakelite. These were used for some time in training exercises and for special applications. However, attempts to reproduce these materials in the early 1970's were unsuccessful. In addition, bakelite, which is fabricated from phenolic-formaldehyde mixtures, has experienced declining usage as newer, less expensive polymer materials have been developed.

Frangible projectiles are also employed as training ammunition in place of kinetic energy penetrators. The simulated projectiles must exhibit similar flight characteristics to the actual penetrators, but ideally self-destruct in flight or on impact for safety reasons (for example, to reduce ricochet). A partially densified iron powder component encased in a low-strength, thermally-degradable plastic container has been used. These replacement projectiles fail on light impact or after heating in flight, thus meeting range safety requirements.

Commercially available non-lead, frangible munitions for training and certification of personnel are presently being fabricated using bullets formed from tungsten and copper powders in a nylon matrix. The projectiles are a direct spin-off from technologies first explored for replacing lead weights used by commercial

fishermen in Europe. The projectiles are formed employing injection molding techniques and various lots have been delivered to various organizations for testing.

5        While the aforementioned ammunition is functional, the density of the bullet material is only approximately half that of the lead-containing components (5.8 versus 11.4 g/cm<sup>3</sup>). The low weight of the projectile causes problems  
10      in weapon functionality and accuracy, especially at extended ranges.

         Another solution being explored is the replacement of lead with other metals such as bismuth. Bismuth metal possesses properties  
15      similar to those of lead. Shotgun ammunition that utilizes bismuth shot is also commercially available, but the density of this metal is only 86% of that of lead (9.8 versus 11.4 g/cm<sup>3</sup>), and again this creates concerns with regards to  
20      ballistic performance.

         In pelletized projectiles, such as shotgun shot, lead has been used for many years in hunting waterfowl and other game birds. Where lead shot has been banned, steel shot has been  
25      required. However, due to the high hardness and strength, and low density (7.5 versus 11.4 g/cm<sup>3</sup>), steels are less desirable choices for use as projectile materials.

         Steel shot has also caused intense  
30      controversy for it is believed that due to its reduced ballistic properties (primarily to the lower density); many birds are being wounded and maimed, dying gruesome deaths. The manufacturers recommend using a steel shot at  
35      least two sizes larger in diameter than lead for the same target and similar distances. This further diminishes effectiveness by decreasing

pattern density (the number of pellets in the shot change).

Although ammunition manufacturers are developing new and improved components for use with steel shot, the ammunition appears to cause excessive wear and undue damage to many shotgun barrels.

Several United States patents have described lead-less or lead-reduced projectiles. For example, U.S. Patent No. 5,264,022 to Haygarth et al. describes a lead-free shotshell pellet made of an alloy of iron and tungsten. The pellets may be coated with a polymeric coating, resin or lubricant.

U.S. Patent No. 4,881,465 to Hooper et al. discloses a non-lead shotgun pellet in which particles made of a first alloy are suspended in a matrix of a second alloy. The first alloy is primarily ferrotungsten, and the second alloy is primarily lead. The second alloy is poured over crushed particles of the first alloy to form the pellets.

U.S. Patent No. 4,498,395 to Kock et al. discloses a powder made of tungsten particles coated with either nickel, copper, silver, iron, cobalt, molybdenum or rhenium, wherein the particle diameters are in the range of 10 to 50  $\mu\text{m}$ . The particles are sintered to form projectiles.

U.S. Patent No. 4,428,295 to Venkataramaraj discloses a high density shot made of a cold-compacted mixture of at least two metal powders. A representative mixture includes 50% lead and 50% tungsten, which is cold pressed in shot molds at 20,000 psi.

It is clear from the above that several attempts have been made in the past to obviate

or diminish the use of lead as a primary material for making projectiles. Yet, no one heretofore has achieved satisfactory performance from non-lead materials.

5     SUMMARY OF THE INVENTION

          An object of the present invention is to provide a projectile which is fully functional and provides characteristics similar to those of standard issue or commercially available analogs  
10     to allow personnel in training to maintain the highest degree of proficiency, to provide the shooter with accurate and dependable munitions, and to eliminate contamination of the environment and to reduce airborne contaminants  
15     in the shooter's breathing zone.

          Another object of the present invention is to provide non-lead, frangible projectiles having ballistic properties and density comparable to existing lead-containing  
20     components.

          Still another object of the present invention is to use a projectile material, the ingredients and processing of which can be varied to provide a controlled or predetermined  
25     impact behavior.

          Yet another object of the present invention is to provide a coated powder which allows for uniform distribution of each constituent material, controlled composition and density,  
30     and tailorable impact behavior through selection of materials, processing conditions, final porosity, and adherence or bonding of the coatings and between particulates.

          These and other advantages of the invention  
35     are achieved by providing projectiles made from blends of metal powders, wherein high density

metals are mixed with lighter and relatively softer metals. The high density metal is preferably heavier than lead, while the softer metal acts as a binder and as a buffer between the high density metal and the steel barrel of a weapon.

To avoid separation of the two metal constituents during handling and processing, the lighter, softer metal may be coated on the heavier metal, and then the coated particles are consolidated through a working process into projectile shapes.

Other objects and advantages which will be subsequently apparent, reside in the details of construction and operation as more fully hereinafter described and claimed, with reference being had to the accompanying drawings forming a part hereof, wherein like numerals refer to like elements throughout.

#### 20 BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a vertical cross-sectional view of a munitions cartridge which includes a bullet or projectile made according to the present invention;

25 Fig. 2 is an enlarged sectional view of a coated particle used to make projectiles according to the present invention;

Figure 3 is a vertical cross-sectional view of a bullet according to the present invention;

30 Figure 4 is a sectional view of a coated shot according to the present invention;

Figure 5 is a side elevational view, partially cut-away, of a shotshell according to the present invention;

Figure 6 is an enlarged cross-sectional view of a shot used in the shotshell of Figure 5; and

Figure 7 is a cross-sectional view of a jacketed bullet according to the present invention.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention provides non-lead frangible projectiles which can be used instead of lead-containing products, thus obviating environmental problems associated with conventional projectiles.

According to one aspect of the present invention, coated metal or metal compound powders and particulates are used as base materials. The projectiles can be constructed to maintain the density and ballistic properties of present lead-containing components, but without using toxic materials. Moreover, the materials can be selected, mixed and processed to achieve controlled impact behavior.

The use of coated particulates allows for uniform distribution of each component, controlled composition and density, and tailorable impact behavior through selection of materials, processing conditions, final porosity, and adherence or bonding of the coatings and between particulates.

In one application of a projectile illustrated in Figure 1, a munitions cartridge 10 includes a casing 12 having a primer 14 at one end and a bullet-receiving opposite end 16.

5 A bullet 18, serving as the "projectile", is fitted into the receiving end 16 of the casing 12. As is standard in the art, a charge of powder 20 contained in the casing 12 is ignited by the primer 14, when acted upon by a firing

10 pin, to propel the bullet 18 down the gun barrel.

According to another aspect of the present invention, the bullet 18 is made by mixing a base constituent, which is heavier than lead,

15 with a binder constituent, which is lighter than lead. The binder constituent is selected to have a degree of malleability and ductility which facilitates formation of a desirable projectile shape when the mixed constituents are

20 subjected to a consolidation process. Toxic materials, such as lead, are not used for either constituent.

The simplest process of fabrication is to blend the base constituent and the binder

25 constituent and then consolidate the blend into projectile shapes using a low energy working technique, such as cold (room temperatur or slightly heated) pressing.

The base constituent is preferably a high density, high hardness powdered material. This constituent may be a metal, metal compound, metal alloy, or mixtures of the aforementioned, and should have a density greater than lead. The binder constituent may also be a metal, metal compound, metal alloy, or mixtures of same, and is softer and less dense than the base constituent.

The higher density base constituent provides mass while the softer, lighter binder constituent acts as a buffer against the steel barrel of a weapon. Prior art projectiles which use lead as a binder do not solve the environmental problem, while those using hard exposed substitutes damage barrels and/or do not have controllable frangibility.

Because metal powders of different density tend to separate during handling and processing, a particular embodiment of the present invention involves coating powders made of the primary (heavier) constituent material with the lighter binder constituent. This is illustrated in Figure 2, wherein a spherical particle 22 made of the primary constituent is coated with a coating 24. The coating 24 is made of the softer, typically lower density binder constituent.

The thickness of the coating 24 and the size of the particle 22 can be selected to control the fraction of each metal in the final component, and thus the density of the projectile. The use of coated powders allows for precise control of composition and results in uniform distribution of each metal throughout the part. In addition, the coating 24 on individual particles 22 ensures that the heavier, harder base constituent, such as tungsten, does not contact and thereby abrade the inside surfaces of the gun barrel.

The coating 24 can be formed in a variety of ways, including fluidized bed and tumbling-bed chemical vapor deposition, electroplating, or other metal deposition processes. A uniform coating of controlled thickness can readily be deposited on powders or particulates of a broad range of sizes and densities.

The coated powders are mixed (if more than one base constituent is used) and pressed, and if necessary, sintered to produce a projectile or other component. The physical properties such as density, hardness, porosity, impact properties, etc. can be controlled through selection of material and powder, particle size, coating material, and coating thickness.

The use of coated powders enhances the ability to control projectile frangibility over a broad range by introducing new variables. These include the bonding of the coating to particle, and particle to particle contact and bonding during consolidation. Thus, projectiles with controllable density and impact properties are fabricated employing coated powders and particulates.

Figure 3 shows a solid body 26 having a desirable projectile shape. The body 26 is illustrated in cross-section, and shows the binder constituent 28 which was not coated on the harder constituent 30. Because the softer binder material 28 flows around the harder constituent 30 under sufficient pressure, the harder constituent 30 is not exposed on the outer surface of the body 26. Thus, the softer material will be in contact with the gun barrel and thereby avoid abrasion from the harder constituent 30.

Figure 4 shows a spherical shot 32 according to the present invention. The shot 32 may consist of a single sphere 34 made of a harder constituent metal, with a coating 36 made of softer, less dense material. While appearing similar in structure to the coated powder of Figure 2, the shot pellet 32 of Figure 4 is a

single sphere, not a pressed agglomeration of powder.

A more preferred form of shot is illustrated in the embodiment of Figures 5 and 6. Referring to Figure 5, a shotshell 38 includes a tube 40 containing a quantity of shot 42, and a head 44 which includes a primer (not shown). The construction of the shotshell 38 is conventional except that the shot 42 is made according to the present invention.

As shown in Figure 6, each shot 42 can be made of a hard constituent material 44 and a relatively soft constituent material 46. The constituent materials can be two powders, or a mixture of powders, selected as per the disclosure herein. Alternatively, the shot 42 could be made by consolidating a coated powder into spherical shapes.

#### Choice of Basic Materials

The base constituent is a powder made of virtually any non-lead material, or mixture of materials, that has a density greater than lead. As noted above, the base constituent may be a metal, metal compound, metal alloy, or a mixture of metals, metal compounds and/or metal alloys. An example of a suitable compound is tungsten

carbide, while suitable elements include  
tungsten and tantalum.

The base constituent materials are typically of relatively high strength and hardness, compared to the binder constituent. This is to ensure that the binder constituent acts as the binder, and not visa versa, and thereby flows to the outer surface of the projectile. This ensures that the softer constituent will form a buffer between the harder base constituent and the gun barrel.

Lead and other toxic materials are specifically excluded as possible base constituents.

The binder constituent is preferably lighter than lead and is softer than the base constituent. Examples of elements capable of use as the binder constituent include, but are not limited to, aluminum, bismuth, copper, tin and zinc, which are environmentally friendly than lead. The binder constituent may be elemental, compounded or alloyed as noted with respect to the base constituent, and may also comprise a mixture of elements, compounds and/or alloys, depending on the physical properties of each and the desired physical properties of the finished product.

### Selective Density and Frangibility

According to the present invention, the choice and ratio of materials can be selected to achieve a desired density and thus ballistic characteristic. Frangibility is controlled through choice and ratio of materials and consolidation technique. Particle size also has a bearing on consolidation and thus contributes to frangibility control. Thus, to obtain a projectile having a density similar to that of a lead-containing equivalent, materials are selected and provided in ranges that produce the desired overall density. To obtain a projectile having, in addition to a desired density, a desired frangibility, a consolidation technique is selected to achieve a desired fracture toughness, or other physical property. For example, an annealing step provided after cold pressing will change the hardness and/or fracture toughness of the projectile. Additionally, frangibility is also a function of the degree of densification (expressed as a percentage of theoretical maximum density) and the type of consolidation technique, such as cold pressing. Powder size will to a certain extent effect the ability to consolidate the powders and the porosity of the end product.

Choices of materials and process conditions to achieve particular examples of projectiles according to the present invention are described in the following examples:

5

Example 1

Tungsten particulates 500-1,000  $\mu\text{m}$  (20-40 mils) in diameter were coated with 50-70  $\mu\text{m}$  (2-3 mils) of aluminum employing a chemical vapor deposition (CVD) technique. A 9.6 g (148 grain) sample of the coated particulates was weighed and placed into the cavity of a cylindrical steel die with a diameter of 0.356 inches. The powder sample was subjected to pressure ranging from 140 to 350 Mpa at room temperature.

Once the chosen pressure was achieved, the pressure was held for approximately 5 seconds to ensure complete compaction. The part was removed from the die as a bullet or "slug" and characterized.

The density of each sample was measured for those pressed at 350 Mpa, the average density of the slugs was 10.9 g/cm<sup>3</sup> or  $\approx$  95% the theoretical density of lead. The room temperature compressive strength of the pressed samples was 145 Mpa, which is adequate for use as

projectiles in small arms, specifically 38 caliber and 9 mm pistols.

### Example 2

Same as Example 1, except for tungsten  
5 carbide spheres, ball point pen balls, with a diameter of 0.051 inches (1.3 mm) were used. A 125  $\mu$ m (5 mil) thick aluminum coating was applied again using a CVD technique. Similar results were achieved as in Example 1.

10

### Example 3

Pellets or shot used in shotguns are made of non-lead materials and have densities to match or approximate lead or lead alloys currently available. The shot has a soft outer  
15 coating which overcomes the problem of steel shot abrading inner surfaces of gun barrels. Basically, the ability of this outer coating to deform, due to its inherent softness compared to steel, is what avoids barrel deformation and  
20 wear.

The properties of the shot are tailored for specific applications. For example, duck and geese hunters require shot with extended range and good penetration. A dense hard pellet would  
25 thus give optimum performance in this application. Target shooters, on the other

hand, prefer light charges of smaller diameter lighter weight shot. This product could permit customized loads and result in improved performance as compared to currently available  
5 ammunition.

It is also possible to include variations in coating or plating of the particulates. More complex combinations of metals, such as ternary compositions, could also be employed.

10 Various combinations of hard and soft materials which are combined to form a shot projectile are shown below in Table I. These have densities matching or approximating pure lead, using metal coated tungsten and tungsten  
15 carbide spheres:

TABLE I

	Materials (core - shell)	Approximate Shot Size (number)	Core Diameter (in)	Coating Thickness (in)
	Tungsten core, various coating materials			
5	W - Al	6	0.090	0.011
	W - Bi	6	0.063	0.026
	W - Cu	6	0.066	0.020
	W - Sn	6	0.074	0.016
	W - Zn	6	0.074	0.016
10	Tungsten carbide core, various coating materials			
	WC - Al	6	0.100	0.007
	WC - Bi	6	0.070	0.019
	WC - Cu	6	0.070	0.015
15	WC - Sn	6	0.090	0.012
	WC - Zn	6	0.090	0.012
	Tungsten core, tin coating, various shot sizes			
	W - Sn	6	0.076	0.01
20	W - Sn	4	0.090	0.019
	W - Sn	2	0.106	0.023
	W - Sn	BB	0.125	0.027
	W - Sn	F	0.152	0.033
25	W - Sn	00	0.230	0.050

Example 4

A mixture of 30 wt. % 320 mesh tin and 70 wt. % 100 mesh tungsten powders was prepared by dry blending the as-received materials. A 9.6 g (148 grain) sample of blended powder was weighed and placed into the cavity of a cylindrical steel die with a diameter of 0.356 inches and placed under the ram of a hydraulic press. The powder sample was subjected to pressures ranging from 140 to 350 Mpa at room temperature. Once the chosen pressure was achieved, the pressure was held for about 5 seconds. The part was removed from the die and characterized.

Density was measured for samples pressed at 350 Mpa, the average density of the slugs was 11.45 g/cm<sup>3</sup> or about 100% the theoretical density of lead. The room-temperature compressive strength of the W-Sn part was about 140 Mpa and the part exhibited almost ductile behavior.

In addition to the cylindrical specimens resembling double-ended wadcutter bullets, truncated cone projectiles of the same diameter and weight (0.356 inches and 148 grains) were also prepared in a similar manner. Ammunition was assembled using the bullets. Pistol ammunition for a 38 caliber revolver with velocities of approximately 900 ft/second was prepared as described in the Speer Reloading manual. The ammunition was fired from a revolver with a 4 inch barrel at an outdoor range. The ammunition using the W-Sn bullets performed as well as similarly constructed ammunition using lead counterparts of similar geometry.

Example 5

Same as Example 3 except for the metal mixture containing 30 wt. % 100 mesh tin and 70 wt. % 100 mesh tungsten. The average density of the parts pressed at 350 Mpa was 11.4 g/cm<sup>3</sup>, 100% that of lead, with an average compressive strength of 130 Mpa, as shown in Table IV.

Example 6

Same as Example 3 except for metal mixture containing 5 wt. % 320 mesh aluminum and 95 wt. % 100 mesh tungsten. The average density of the parts pressed at 350 Mpa was 10.9 g/cm<sup>3</sup>, which is 96% that of lead, with an average compressive strength of 200 Mpa, as shown in Table IV.

Example 7

Same as Example 3 except for metal mixture containing 20 wt. % 320 mesh copper and 80 wt. % 100 mesh tungsten. The average density of the parts pressed at 350 Mpa was 11 g/cm<sup>3</sup>, 97% that of lead, with an average compressive strength of 220 Mpa.

Example 8

Same as Example 3 except for the metal mixture containing 40 wt. % 100 mesh zinc and 60 wt. % 100 mesh tungsten. The average density of the parts pressed at 350 Mpa was 10.9 g/cm<sup>3</sup>, 96% that of lead, with an average compressive strength of 145 Mpa.

Example 9

5 Same as Example 3 except for metal mixture containing 70 wt. % 100 mesh bismuth and 30 wt. % 100 mesh tungsten. The average density of the parts pressed at 350 Mpa was 10.9 g/cm<sup>3</sup>, 96% that of lead.

10 Materials for use as the high density constituent include tungsten, tungsten carbide, tantalum, and any non-lead metals, metal alloys or other materials with similar densities. Coating metals include aluminum, bismuth, copper, tin, zinc, and other non-lead metals  
\* { with similar properties. Density and  
15 frangibility can be customized for individual needs, by considering the density and mechanical properties of the individual constituents. The following Tables II and III serve as guidelines for material selection:

TABLE II

	Material	Symbol	Density (g/cm <sup>3</sup> )	Modulus (GPa)	Strength (MPa)	Hardness (VHN)
	Lead	Pb	11.36	14	13	0.049
5	Lead + 0.01 % Tin	Pb/Sn	11.34	14	18	5 HB*
	Lead + 5 % Tin	Pb/Sn	11.00		23	8 HB*
	Lead + 20 % Tin	Pb/Sn	10.20		40	11.3HB
	Lead + 50 % Tin	Pb/Sn	8.89		42	14.5 HB*
10	Lead + 4 % Antimony	Pb/Sb	11.02		100	8.1HB*
	Copper	Cu	8.93	130	200	0.50
	Bismuth	Bi	9.81	32	NA	0.095
	Gold	Au	19.30	78	100	0.66
15	Silver	Ag	10.49	70	125	0.94
	Platinum	Pt	21.45	170	140	0.86
	Aluminum	Al	2.70	60	45	0.25
	Tungsten	W	19.25	415	3450	3.43
	Tin	Sn	7.29	15	15	0.071
20	Iron	Fe	7.87	170	600	0.65
	Molybdenum	Mo	10.22	310	500	0.38
	Niobium	Nb	8.57	100	275	0.86
	Tantalum	Ta	16.6	190	360	1.06
	Titanium	Ti	4.51	200	235	1.54
25	Low Carbon Steel	Fe-FeC	7.5	200	350	90 HB*
	Tungsten Carbide	WC	15.0	640	1500	18.44
	Zinc	Zn	7.13	70	135	0.02

\* The hardness of lead is 3 HB in similar units.

TABLE III

Material	Symbol	Health Rating	Comments from "Sax and Lewis"	MSDS Acute Exposure	MSDS Chronic Exposure	TLV/TWA (mg/m <sup>3</sup> )
Lead	Pb	4	poison, carcinogen, teratogen, lead poisoning most common of occupational diseases	numerous difficulties, see MSDS	see MSDS	0.07 -0.2 (0.05)
Copper	Cu	4	metal and powder not problems, fumes only	ulcers, pneumonia	anemia	NA (1)
Bismuth	Bi	1	industrially not considered toxic	mild irritant	nervous systems	NA (NE)
Gold	Au	3	none			NA
Silver	Ag	3	skin pigmentation effects			0.1
Aluminum	Al	1	dust possibly associated with pulmonary fibrosis, Alzheimer's	mild irritant	Alzheimer's	10 (10)
Tungsten	W	2	industrially not considered toxic	NISS	HM disease pneumonia	5 (5)
Tin	Sn	2	not considered toxic	mild irritant	pneumonia	2 (2)
Iron	Fe	2	as dust can be irritant and possibly poisonous	oxide dust irritant	oxide mottling of lungs	NA (5)
Tantalum	Ta	3	considered nontoxic, industrial poisoning not recorded			5.0
Titanium	Ti	1	considered physiological inert	nuisance	irritant	NA (NE)
Molybdenum	Mo	1	human poisoning by inhalation not been documented	irritant	pneumonia	15
Low carbon Steel	Fe-FeC	2	see iron and other steel additives			10
Zinc	Zn	2	dust and powder nontoxic to humans	NISS	dermatitis	NA (10)

Table IV shows a variety of processed projectiles having a range of densities from 90 to 120% of lead and acceptable mechanical properties, as described in Examples 3-8 above. It is apparent from the above data that the physical properties of the shot or bullets can be varied by changing the parameters of the

powder compositions. For example, mesh size, densification pressure and ratio of hard to soft metals can be varied to derive a desired degree of frangibility.

TABLE IV

Composition	Fraction (by wt)	Processing Pressure (MPa)	Density (g/cm <sup>3</sup> )	% Density of Lead	Compressive Strength (MPa)
Pb	100	na	11.36	100.0	
Pb-Sn	95/5	na	11.00		
Pb-Sn	80/20	na	10.20		
W-Sn	70/30	140	10.17	89.2	70
"		210	10.88	95.8	95
"		280	11.34	99.9	127
"		350	11.49	101.2	137
W-Sn*	58/42	140	9.76	85.9	84
"		210	10.20	89.8	95
"		280	10.49	92.3	106
W-Al II	95/5	140	9.35	82.3	57
"		210	10.06	88.6	101
"		280	10.62	93.5	157
"		350	10.91	96.0	200
W-Zn	60/40	350	10.85	95.5	145
Bi-W	70/30	350	10.88	95.8	not tested
W-Cu	80/20	350	10.99	96.8	220

Compressive strengths of lead and lead tin alloys are in a range from 15 to 70 MPa. Densities of lead and lead-tin alloys are in a range from  $\approx 10.70$  to  $11.36 \text{ g/cm}^3$  (pure lead).

Non-lead projectiles according to the present invention are formed using powder metallurgy techniques. Controlling density permits matching of any lead, lead alloys, or copper/lead construction being employed in current bullets. With matched density, the present projectiles have equivalent or comparable weapon function, ballistic properties, and accuracy. The impact behavior of the projectiles is also controllable through changes in composition and processing. Components with a broad range of frangibility or impact properties can be fabricated thus meeting the needs of many users for a wide variety of applications. Processing is simple, involving only the cold pressing of powders.

The use of coated powders improves reproducibility and uniformity, and prevents wear of barrels by preventing contact by the harder high density metal. Sintering may permit a greater level of flexibility in compositions and properties.

The projectiles described herein could replace any bullet in current use that employ lead or other hazardous materials. This would benefit any organization and individual that uses ammunition for training, self defense, police applications, military, hunting, sport shooting, etc. Moreover, the term "projectile" refers to any munitions round, or the core to a munitions round. For example, the projectiles of the present invention could be the core of a jacketed round.

An example of a jacketed round can be found in Figure 7, wherein a bullet 48 has an outer jacket 50, made of suitable jacketing material

(typically, copper is used as a jacket material, although other non-traditional materials may be desirable for environmental reasons), and an inner core 52 made of the non-lead materials described herein. The amount, mixture and type of materials are selected according to the desired ballistic properties of the projectile as per the present invention. Also, the forming techniques can be such that the core is preformed or formed in the jacket as by swaging. In either event, the amount of consolidation is controlled to achieve desired frangibility characteristics.

The projectiles encompassed in the present invention could include, in addition to bullets, virtually any type of artillery round, such as those capable of exploding on impact (and thus incorporating an explosive charge), a hand grenade, a rocket warhead, etc.

Objects other than munitions projectiles also could be fashioned from the aforementioned materials and techniques. For example, non-lead fishing weights, tire balance weights, or ship's ballast could be made using the present invention. Other uses are easily envisioned, where it is desirable to emulate mechanical and physical properties of a material which is to be replaced, either due to the scarcity or toxicity of the replaced material.

The many features and advantages of the invention are apparent from the detailed specification, and thus, it is intended by the appended claims to cover all such features and advantages of the invention which fall within the true spirit and scope of the invention. Further, since numerous modifications and variations will readily occur to those skilled

in the art, it is not desired to limit the invention to the exact construction and operation illustrated and described, and accordingly, all suitable modifications and  
5 equivalents may be resorted to, falling within the scope of the invention.

WHAT IS CLAIMED IS:

1. A projectile comprising:  
a base constituent having a density higher than lead; and
- 5 a lead-free binder constituent made of a metallic phase and having sufficient malleability and ductility to bind together with the base constituent into a solid body of desired shape when subjected to a consolidation force.
2. A projectile according to claim 1, wherein the base constituent is a powder, and the binder constituent is coated on the base constituent.
3. A projectile according to claim 1, wherein the base constituent is one of a metal, metal alloy, metal compound, and a mixture of metals, metal alloys and metal compounds.
4. A projectile according to claim 3, wherein the base constituent is made of a material selected from the group consisting of tungsten, tungsten carbide, tantalum.
5. A projectile according to claim 1, wherein the binder constituent is one of a metal, metal alloy, metal compound, and a mixture of metals, metal alloys and metal compounds.

6. A projectile according to claim 5, wherein the binder constituent is selected from the group consisting of aluminum, bismuth, copper, tin, and zinc.

7. A projectile according to claim 1, wherein the base constituent and the binder constituent are made of materials and provided in ratios selected to achieve a desired density of the solid body.

8. A projectile according to claim 7, wherein the solid body has a theoretical density substantially similar to that of lead.

9. A projectile according to claim 1, wherein the base constituent and the binder constituent are made of materials, provided in ratios, and subjected to consolidation process parameters selected to achieve a desired density and frangibility of the solid body.

10. A projectile according to claim 1, wherein the base constituent is made of a material selected from the group consisting of tungsten, tungsten carbide, and tantalum, and the binder constituent is selected from the group consisting of aluminum, bismuth, copper, tin, and zinc.

11. A projectile according to claim 1, wherein the base constituent is tungsten and the binder constituent is aluminum.

12. A projectile according to claim 1, wherein the base constituent is a tungsten powder having

a diameter in the range of 500-1,000  $\mu\text{m}$ , and the binder constituent is aluminum coated on each powder particle, each coating having a thickness of between 50-70  $\mu\text{m}$ .

13. A projectile according to claim 1, wherein the amount of the base constituent relative to the binder constituent is about 1-99 weight percent.

5 14. A projectile according to claim 1, wherein the base constituent is one of a powder and a mixture of powders, and the binder constituent is one of a powder and a mixture of powders, the base constituent and the binder constituent being evenly distributed to form a blend prior to consolidation.

15. A projectile according to claim 14, wherein the base constituent comprises 1-99 weight percent of the blend.

16. A projectile according to claim 1, wherein the base constituent is a tungsten powder and the binder constituent is a tin powder.

17. A projectile according to claim 16, wherein the base constituent and the binder constituent are evenly distributed to form a blend prior to consolidation, and the blend comprises about 70 weight percent tungsten and the remainder tin.

18. A projectile according to claim 17, wherein the tungsten powder is about 100 mesh and the tin powder is about 320 mesh.

19. A projectile according to claim 17, wherein the tungsten powder is about 100 mesh and the tin powder is about 100 mesh.

20. A projectile according to claim 1, wherein the base constituent is a tungsten powder and the binder constituent is an aluminum powder.

21. A projectile according to claim 16, wherein the base constituent and the binder constituent are evenly distributed to form a blend prior to consolidation, and the blend comprises about 95  
5 weight percent tungsten powder and the remainder aluminum powder.

22. A projectile according to claim 21, wherein the tungsten powder is about 100 mesh and the aluminum powder is about 320 mesh.

23. A projectile according to claim 1, wherein the base constituent is tungsten and the binder constituent is copper.

24. A projectile according to claim 23, wherein the base constituent and the binder constituent are evenly distributed to form a blend prior to consolidation, and the blend comprises about 80  
5 weight percent tungsten and the remainder copper.

25. A projectile according to claim 23, wherein the tungsten is a 100 mesh powder and the copper is a 320 mesh powder.

26. A projectile according to claim 1, wherein the base constituent is tungsten and the binder constituent is zinc.

27. A projectile according to claim 22, wherein the base constituent and the binder constituent are evenly distributed to form a blend prior to consolidation, and the blend comprises about 60 weight percent tungsten and the remainder zinc.

28. A projectile according to claim 27, wherein the tungsten is a 100 mesh powder and the zinc is a 100 mesh powder.

29. A projectile according to claim 1, wherein the base constituent is tungsten and the binder constituent is bismuth.

30. A projectile according to claim 29, wherein the base constituent and the binder constituent are evenly distributed to form a blend prior to consolidation, and the blend comprises about 30 weight percent tungsten and the remainder bismuth.

31. A projectile according to claim 29, wherein the tungsten is a 100 mesh powder and the bismuth is a 100 mesh powder.

32. A method of making a projectile comprising the steps of:

combining a base constituent having a density greater than lead with a lead-free binder constituent made of a metallic phase to form a blend; and

consolidating the blend to thereby form a solid body of desired shape,

the binder constituent having sufficient malleability and ductility to bind together with the base constituent and thereby form the solid body when subjected to the consolidation force.

33. A method according to claim 32, wherein the base constituent is a powder, and the combining step comprises forming a coating made of the binder constituent on the powder constituent.

34. A method according to claim 33, wherein the forming step comprises forming a coating on the powder constituent by a process selected from the group consisting of plating, dipping,  
5 coating by chemical vapor deposition, and coating by fluidized bed treatment.

35. A method according to claim 32, wherein the consolidating step comprises cold pressing the blend.

36. A method according to claim 32, further comprising sintering the solid body after the consolidating step.

37. A method according to claim 32, wherein the consolidating step comprises placing the blend in a die and cold pressing the blend with sufficient pressure to achieve a desired degree of densification of the blend.

38. A method according to claim 32, wherein the base constituent is one of a powder and a mixture of powders, and the binder constituent is one of a powder and a mixture of powders, and  
5 the combining step comprises blending the binder constituent and the base constituent to form the blend.

39. A munitions cartridge comprising:

a casing having a primer disposed at one end and an opposite, bullet-receiving end and containing a charge between the two ends; and

5 a bullet mounted in the bullet-receiving end of the casing, the bullet comprising a base constituent having a density higher than lead; and

10 a lead-free binder constituent made of a metallic phase and having sufficient malleability and ductility to bind together with the base constituent into a solid body of desired shape when subjected to a consolidation force.

40. A munitions cartridge according to claim 39, wherein the binder constituent is coated on the base constituent.

41. A munitions cartridge according to claim 39, wherein the base constituent is made of a material selected from the group consisting of tungsten, tungsten carbide, and tantalum.

42. A munitions cartridge according to claim 39, wherein the binder constituent is selected from the group consisting of aluminum, bismuth, copper, tin, and zinc.

5 43. A munitions cartridge according to claim 39, wherein the base constituent is made of a material selected from the group consisting of tungsten, tungsten carbide, and tantalum, and the binder constituent is selected from the group consisting of aluminum, bismuth, copper, tin, and zinc.

44. A munitions cartridge according to claim 39, wherein the base constituent is tungsten and the binder constituent is aluminum.

45. A munitions cartridge according to claim 35, wherein the base constituent and the binder constituent are made of materials and provided in ratios selected to achieve a desired density of the solid body.

46. A munitions cartridge according to claim 35, wherein the base constituent and the binder constituent are made of materials, provided in ratios, and subjected to consolidation process parameters selected to achieve a desired density and frangibility of the solid body.

47. A projectile comprising:

a substantially spherically shaped inner body made of a first material having a density greater than lead; and

5 an outer coating formed on the body and being made of a second, metallic phase material having a density less than lead and a strength and hardness less than steel, to thereby avoid damage to a steel gun barrel.

48. A projectile according to claim 47, wherein the first material is selected from the group consisting of tungsten, tungsten carbide, and tantalum, and the second material is selected from the group consisting of aluminum, bismuth, copper, tin and zinc.

49. A weight comprising:

a base constituent having a density higher than lead; and

a lead-free binder constituent made of a metallic phase and having sufficient malleability and ductility to bind together with the base constituent into a solid body of  
5 desired shape when subjected to a consolidation force.

50. A weight according to claim 49, wherein the base constituent is a powder, and the binder constituent is coated on the base constituent.

51. A weight according to claim 49, wherein the base constituent is one of a metal, metal alloy, metal compound, and a mixture of metals, metal alloys and metal compounds.

52. A weight according to claim 49, wherein the base constituent is made of a material selected from the group consisting of tungsten, tungsten carbide, tantalum.

53. A weight according to claim 49, wherein the binder constituent is one of a metal, metal alloy, metal compound, and a mixture of metals, metal alloys and metal compounds.

54. A weight according to claim 53, wherein the binder constituent is selected from the group consisting of aluminum, bismuth, copper, tin, and zinc.

55. A weight according to claim 49, wherein the base constituent and the binder constituent are made of materials and provided in ratios selected to achieve a desired density of the solid body.

56. A weight according to claim 55, wherein the solid body has a theoretical density substantially similar to that of lead.

57. A weight according to claim 49, wherein the base constituent and the binder constituent are made of materials, provided in ratios, and subjected to consolidation process parameters  
5 selected to achieve a desired density and frangibility of the solid body.

58. A weight according to claim 49, wherein the base constituent is made of a material selected from the group consisting of tungsten, tungsten carbide, and tantalum, and the binder  
5 constituent is selected from the group consisting of aluminum, bismuth, copper, tin, and zinc.

59. A shotshell comprising:  
a tube having first and second opposite axial ends;  
a head disposed at one of the first and  
5 second opposite axial ends of the tube; and  
at least one shot having a base constituent having a density higher than lead, and a lead-free binder constituent made of a metallic phase and having sufficient malleability and ductility  
10 to bind together with the base constituent into a solid body of desired shape when subjected to a consolidation force.

60. A shotshell according to claim 59, wherein the base constituent and the binder constituent are made of materials, provided in ratios, and subjected to consolidation process parameters  
5 selected to achieve a desired density and frangibility of the solid body.

61. A shotshell according to claim 59, wherein

the base constituent is made of a material selected from the group consisting of tungsten, tungsten carbide, and tantalum, and the binder constituent is selected from the group  
5 consisting of aluminum, bismuth, copper, tin, and zinc.

62. A projectile comprising:  
an outer jacket; and  
an inner core disposed at least partially within the outer jacket, the core having a base  
5 constituent having a density higher than lead, and a lead-free binder constituent made of a metallic phase and having sufficient malleability and ductility to bind together with the base constituent into a solid body of  
10 desired shape when subjected to a consolidation force.

63. A shotshell according to claim 62, wherein the base constituent and the binder constituent are made of materials, provided in ratios, and subjected to consolidation process parameters  
5 selected to achieve a desired density and frangibility of the solid body.

64. A shotshell according to claim 62, wherein the base constituent is made of a material selected from the group consisting of tungsten, tungsten carbide, and tantalum, and the binder  
5 constituent is selected from the group consisting of aluminum, bismuth, copper, tin, and zinc.

FIG. 1

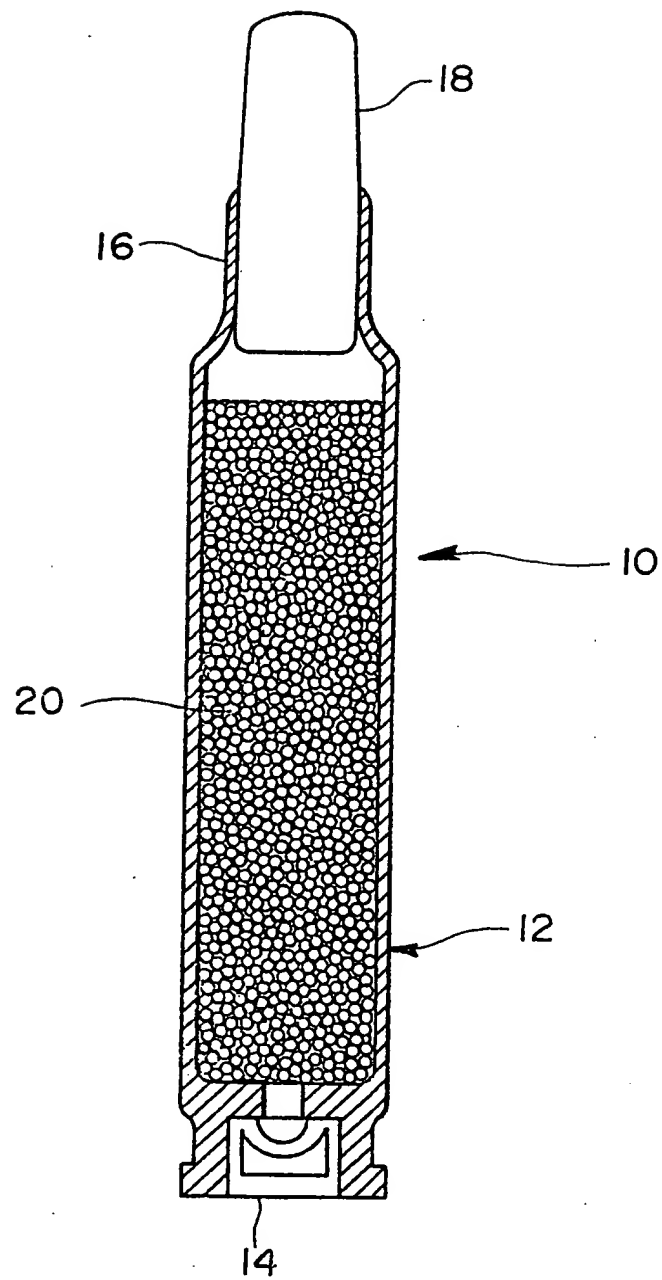


FIG. 2

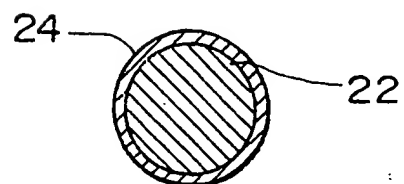


FIG. 3

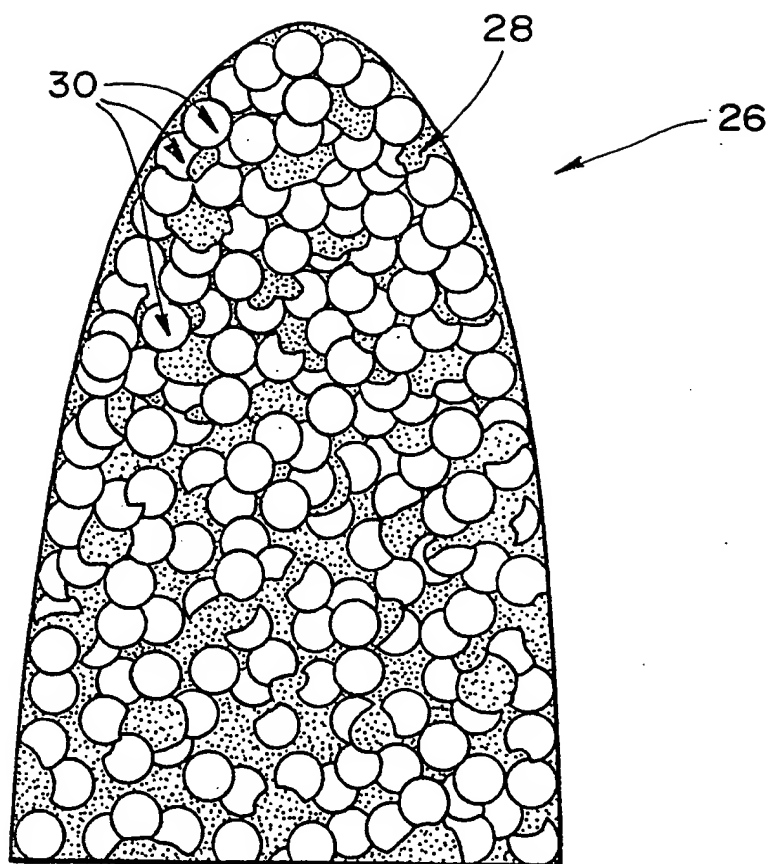


FIG. 4

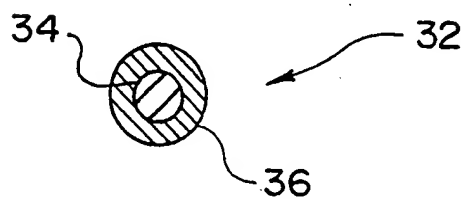


FIG. 5

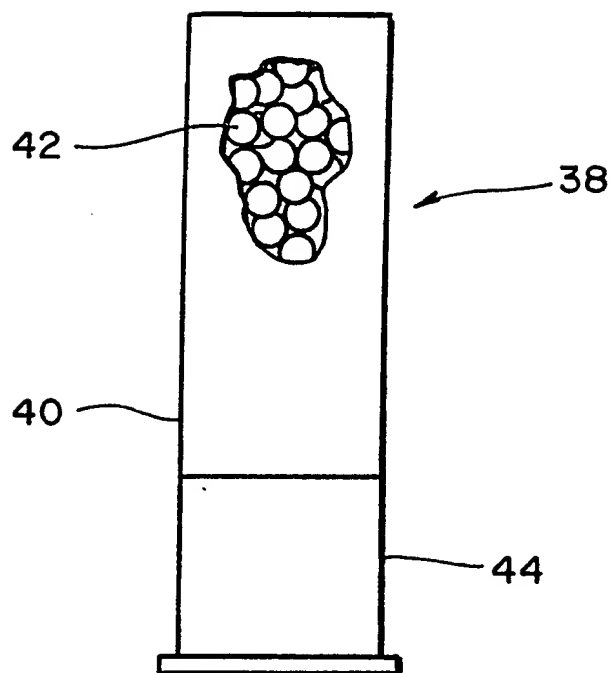


FIG. 7

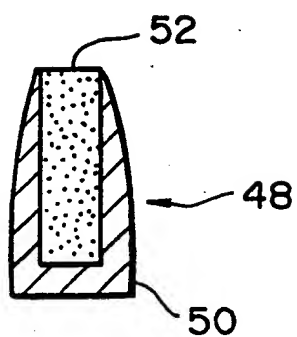
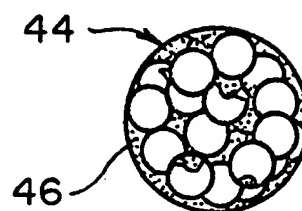


FIG. 6



## INTERNATIONAL SEARCH REPORT

national application No.  
PCT/US95/08165

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : F42B 12/02

US CL : 102/517

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : Please See Extra Sheet.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X, P	US, A, 5,399,187 (MRAVIC ET AL) 21 March 1995, see entire document.	1, 3 - 11, 14, 16, 20, 23, 26, 29, 32, 35-38, 62-66
----- Y		----- 2, 12, 13, 15, 17-19, 21, 22, 24, 25, 27, 28, 30, 31, 33, 34, 39-46, 49-58, 66
Y	US, A, 4,981,512 (KAPOOR) 01 January 1991, see entire document.	2, 12, 3, 34

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	&*	document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means		
*P* document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

12 SEPTEMBER 1995

Date of mailing of the international search report

12 OCT 1995

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
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# INTERNATIONAL SEARCH REPORT

national application No.  
PCT/US95/08165

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X — Y	US, A, 5,279,787 (OLTROGGE) 18 January 1994, see entire document.	1,3-8,10, 11,14,16, 20,23,26, 29,32,35- 38,62-65 -----  2,9,12,13, 15,17-19, 21,22,24, 25,27,28, 30,31,33, 34,39-46, 49- 61,66
Y	US, A, 2,840,944 (THOMPSON) 01 July 1958, see Figures 8 and 9.	39-46, 59-61
X	US, A, 5,088,415 (HUFFMAN ET AL) 18 February 1992, see col. 2 lines 29-38.	47 and 48
Y	US, A, 4,949,645 (HAYWARD ET AL) 21 August 1990, see the Abstract, col. 1, lines 15-25.	49-58
A	US, A, 5,069,869 (NICOLAS ET AL) 03 December 1991.	
A	WO, A, 94 11697 (PERSSON) 26 May 1994.	

# INTERNATIONAL SEARCH REPORT

..national application No.  
PCT/US95/08165

## B. FIELDS SEARCHED

Minimum documentation searched

Classification System: U.S.

102/448, 459, 501, 506, 514, 516, 517, 529; 43/42, 39, 44.87, 449;  
419/30, 32, 35, 38

## B. FIELDS SEARCHED

Electronic data bases consulted (Name of data base and where practicable terms used):

APS Text

- L1 Fishing Weight #
  - L2 Fishing (2A) Weight II
  - L3 L2 and Tungsten
  - L4 L2 and Tantalum
  - L5 Tungsten and 43/class
  - L6 Tantalum and 43/class
  - L7 L5 or L6
  - L8 Tungsten Carbide and 43/class
  - L9 L5 or L8
  - L10 L3 or L5 or L6
  - L11 Weight and Tungsten
  - L12 L11 and Fish?
  - L13 L12 and Bismuth
  - L14 L13 and Copper
  - L15 L14 and Tin
  - L16 L15 and Zinc
- 
- L1 Projectile # or Bullet # or Penetrator #
  - L2 419/30, 32, 35 and 38
  - L3 L1 and L2
- 
- L1 419/35/CCLST
  - L2 Projectile II or Bullet II
  - L3 L1 and 2
  - L4 Tungsten #
  - L5 L1 and L4
  - L6 L5 and Copper
  - L7 L1 not L5

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US95/08165

## B x I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:  
Please See Extra Sheet.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐

The additional search fees were accompanied by the applicant's protest.

☒

No protest accompanied the payment of additional search fees.

**BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING**

This ISA found multiple inventions as follows:

First grouping, claims 1-48 and 59-64, drawn to a projectile and a method of making a projectile, classified in class 102, subclass 439.

Group I, the species of Figures 1 and 3, claims 1-11, 13-32, 35-39, 41-46.

Group II, the species of Figure 4, claims 47 and 48.

Group III, the species of Figure 6, claims 1-46, 59, 60, 61.

Group IV, the species of Figure 7 claims 1-11, 13-32, 35-39, 41-46, 62-64.

Group V, claims 49-58, drawn to a weight classified in class 43, subclass 44.87.

Group I-IV lack unity from Group V because they are mutually distinct inventions.

Groups I-IV are directed to distinct species of the invention. There are no common features among the species which avoid the prior art.